

Impact of natural and anthropogenic pyrogenic Carbon in Mediterranean ecosystems



Editors:

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IMPACT OF NATURAL AND ANTHROPOGENIC PYROGENIC CARBON IN MEDITERRANEAN ECOSYSTEMS

Book of Abstracts of the communications presented to the European Science Foundation-Exploratory Workshop “Impact of natural and anthropogenic pyrogenic Carbon in Mediterranean ecosystems”, Seville-Spain. November 5th-7th, 2013.



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PROLOGUE

In Mediterranean ecosystems, charred vegetation residues derived from incomplete combustions (natural wildfires and prescribed burning) play an important role in ecology and as an archaeological record. After its incorporation into the soil this pyrogenic organic matter (PyOM) or as it is also called “Black Carbon” may have considerable contribution to its organic matter (OM) pool. In addition, during the last years, the fertilizing properties of charred plant residues were re-discovered and are nowadays divulged and encouraged within the concept of using biochars produced in a low/no oxygen environment (pyrolysis conditions) as soil amendment. The long-term impact of this practice as well as that of burning harvest residues on soil properties and on soil OM quality has not been well studied and therefore doubts persist. Thus, the present exploratory workshop entitled “Impact of natural and anthropogenic pyrogenic Carbon in Mediterranean ecosystems” is a clear consequence of the international growing interest in solving these key questions. Which are strongly demanded to be answered by the scientific community, Mediterranean farmers as well as public agents and stakeholders.

The role of PyOM derived from incomplete biomass combustion in biogeochemical cycles has received much attention during last decades. In addition to its role as effective sorbent and viable soil amendment, several forms of PyOM are widely recognized as an important carbon sink in the global carbon cycle. The significance of PyOM as a carbon sink is based on its assumed relatively high recalcitrance to both abiotic and biotic degradation. Research on the environmental degradability of PyOM have suggested turnover times ranging from decades to millennia but other studies indicated shorter mean residence times. However, In general, slow turnover rates and high carbon contents have led to increased interest in land application of engineered PyOM materials, so called “biochars” as a key component in an integrative strategy for carbon sequestration to mitigate global climate change. Estimated carbon sequestration potential in these biochars range as high as 9.5 Pg C yr^{-1} which is of the same magnitude as current emissions estimates from fossil fuels. The inherent variability of biochars (stemming from different feedstocks and production conditions) coupled with that of soils to which they are applied implies a high variability of the effect of those materials on soil properties and productivity. This strongly suggests that the production and use of biochars, as a carbon sequestration strategy, will need to be customized for each situation. However, biochar effects on different ecosystems or in the food chain have been assessed poorly, particularly under different climatic conditions, soil types and land management systems. A major problem of present biochar research is that available data are mostly related to initial biochar effects. However, many long-term impacts may be

extrapolated from observations made during the investigation of ecosystems affected by natural fires. On the other hand the strong efforts presently conducted to increase our knowledge about the fate of biochar in soils can serve for scientists which are seeking a better understanding of the ecological impact of vegetation fires. Thus the goal of the workshop is to supply a platform for experts of both research fields for fruitful discussions and interchange of information. This strategy may help to improve the coordination of joint research and to avoid the repetition of experiments while other urgently needed investigations are not yet performed due to lack of (research) resources and coordination.

This Exploratory Workshop funded by the European Science Foundation and organised by the “Geoecología, Biogeoquímica y Microbiología Ambiental” Department of the “Instituto de Recursos Naturales y Agrobiología de Sevilla” (IRNAS-CSIC) is intended to permit the initiation of close collaborations between leading researchers from different european institutions and also with the network eBRN (European Biochar Research Network) of the COST Action to form a multidisciplinary team. As a starting point, a joint compilation of studies addressing important key questions concerning natural PyOM and biochar can be found on the next pages: The latter includes, i) the chemical composition and structure of the different forms of PyOM (including BC and biochar); ii)-chemical and biological recalcitrance of PyOM together with mechanisms of stability and functionality as well as the carbon sequestration potential and iii) the impact of PyOM in different Mediterranean soils.

With this we hope to start new and helpful discussions leading to novel and successful ideas and cooperations in both research fields.

José M. de la Rosa & Heike Knicker, Editors.

IRNAS-CSIC, Reina Mercedes Av, 10. 41012, Seville, Spain.

ORGANIZATION OF THE ESF EXPLORATORY WORKSHOP: IMPACT OF NATURAL AND ANTHROPOGENIC PYROGENIC CARBON IN MEDITERRANEAN ECOSYSTEMS

Convenor: José María de la Rosa

Co-convenor: Heike Knicker

Consejo Superior de Investigaciones Científicas (CSIC)

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ORAL PRESENTATIONS

Session 1. Pyrogenic C: Distribution and stability

WHERE DOES ALL THE PYROGENIC CARBON GO? ITS REDISTRIBUTION IN THE ENVIRONMENT

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Vegetation fires currently affect 330-430 Mha of the global land surface every year. All fires produce pyrogenic carbon (PyC), with the conversion rate of fuel to PyC depending on fuel characteristics and burning conditions. It is well established that PyC exhibits an enhanced recalcitrance compared to its organic source material and the production of PyC can, therefore, be seen as a form of medium-term carbon sequestration, particularly where the vegetation consumed during fire recovers rapidly. Much of the research on the fate of PyC in the environment has focused on locations where it has been incorporated into soils *in-situ* or its deposition in marine sediments as ultimate sinks. The significance of post-fire transport of PyC and its redistribution within terrestrial environments, however, has been largely overlooked.

Post-fire landscapes are very susceptible to erosion due to the loss of protective vegetation and litter cover and the commonly observed reduction in soil stability and infiltration capacity, which further enhances runoff and erosion during rainfall. The low density of PyC makes it highly susceptible to both wind and water erosion and its often hydrophobic nature is likely to facilitate floating during water erosion. In the Mediterranean and many regions elsewhere, areas with significant topography are often those under dense vegetation cover, and hence most susceptible to fire, to high PyC production, and its subsequent redistribution by erosion (Fig. 1 A, B). Its accumulation at off-site depositional sites can be substantial (Fig. 1 A, C, D) and its rate of degradation is likely to be reduced further due to burial.

To date, PyC fluxes by post-wildfire erosion have been poorly quantified and empirical relations between soil erosion and PyC movement need yet to be established. Knowledge of its erodibility, transport behavior, fluxes and the nature of its deposition sites is essential in understanding the ultimate role of PyC as a long-term C sink.

Substantial efforts are already being made by the soil science and geomorphology communities to measure and model post-fire soil erosion and sediment fluxes, but the material is usually considered as a whole and little is known about the quantities and types of PyC redistributed within these fluxes. In addition, little is known about the fate of PyC removed from burned sites in dissolved form. In this presentation, we discuss, with a particular focus on Mediterranean environments, the

- (i) properties of PyC that are relevant in its redistribution;
- (ii) relative importance of the various processes leading to its redistribution;
- (iii) likely quantities of PyC available for redistribution for various environments; and
- (iv) suggest ways to address the knowledge gap that currently exists on the quantities, pathways and fate of PyC in the environment.

A more complete understanding of PyC production, post-fire redistribution and ultimate burial is essential to determine the role of PyC in the global carbon cycle.

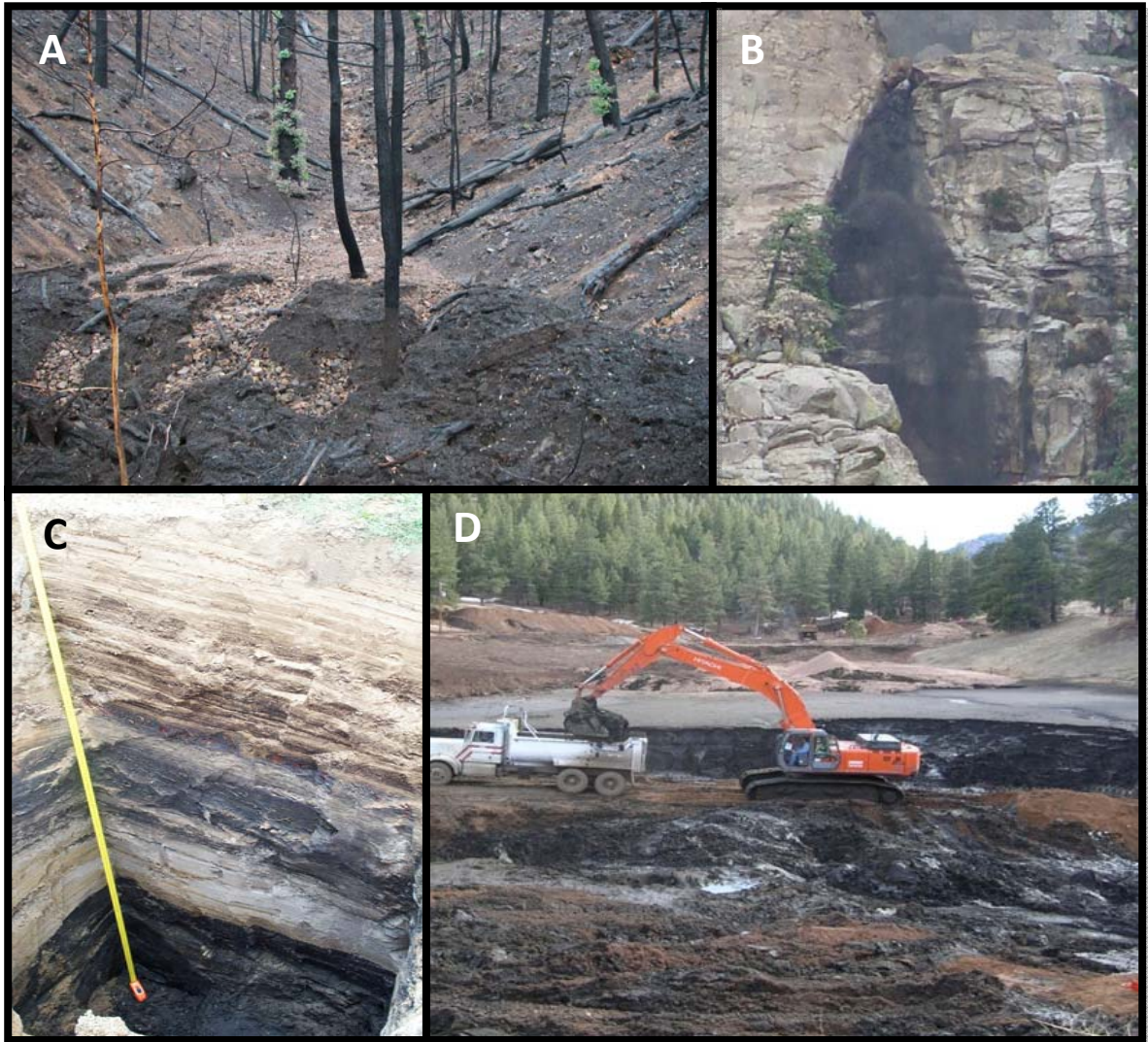


Figure 1. (A) Ash and PyC footslope deposits 4 months after the catastrophic Australian 2009 *Black Saturday* fire (Photo: S. Doerr). (B) Ash and PyC offsite transport after wildfire in Arizona (Photo: R. Smith). (C) PyC-rich layers in Mediterranean soil (Photo: A. Cerda). (D) Excavation of PyC-rich material deposited offsite following its fluvial erosion at a wildfire affected area upstream (Photo: G. Baxter).

DEGRADATION VERSUS STABILITY: UNDERSTANDING THE SOURCE, FATE AND AGE OF PYROGENIC CARBON IN THE ENVIRONMENT

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Pyrogenic carbon (PyC) from incomplete biomass combustion has global prevalence, with an estimated 50-200 Tg of new PyC entering atmospheric, aquatic and terrestrial carbon reservoirs every year (Kuhlbusch and Crutzen, 1995). PyC is also frequently described as one of the most recalcitrant forms of environmental carbon, with estimated soil residence times on the order of 10^3 years (Glaser et al., 2001; Preston and Schmidt, 2006), forming a significant global carbon sink. Yet PyC remains a very poorly understood and poorly quantified factor in global biogeochemical cycles; current stocks and fluxes of some PyC components have high associated uncertainties of over $\pm 50\%$ on global scales (e.g. Ramanathan and Carmichael, 2008), much of which can be attributed to measurement uncertainties. Better understanding of PyC behavior in the environment is crucial. Such understanding will inform efforts to offset anthropogenic fossil fuel emissions of 5.4 Pg C yr^{-1} via biochar soil amendments, and allow us to accurately factor PyC in to both predictive and retrospective models of global carbon budgets. The last point is critical, as data now shows mineralization of at least some PyC to CO_2 over annual timescales, meaning PyC cycling could be much faster than previously thought (Zimmermann *et al.*, 2012). In addition, climate change is certain to affect BC production and turnover rates, but the likely magnitude and nature of these changes remain imperfectly understood.

Here, we discuss key knowledge gaps surrounding the source, fate, and turnover time of PyC in the environment, and present new results from studies aimed at addressing these gaps. This work focuses on understanding the factors controlling the degradation versus stability of PyC in the environment, and draws on a range of methodological approaches. These include hydropyrolysis, a relatively new technique in PyC investigations, which separates highly recalcitrant 'Black Carbon' from more labile material in PyC samples (Meredith et al., 2012). Results show that chemical and physical modifications of PyC occur rapidly upon environmental exposure ($<1\text{yr}$), and that the magnitude and nature of these changes is dominantly controlled by three factors; the chemistry of the starting PyC, the temperature of PyC production, and the environment of deposition. Starting material affects the proportion of recalcitrant versus labile carbon structures in PyC. Environmental alteration is more dramatic and rapid for PyC produced at lower temperatures ($\sim 300^\circ\text{C}$), and is modulated by ambient temperature, soil moisture content and pH. Finally, approaches to understanding PyC behaviour in the environment are discussed, including the possibilities and benefits of integrated methodologies.

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CHEMICAL, PHYSICAL AND BIOLOGICAL STABILITY OF PYROGENIC ORGANIC MATTER IN SOIL

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In view to evaluate the C sequestration potential of pyrogenic C in soil, the objective of our study was to use a combination of physical, chemical and biological methods to identify physical and chemical properties determining their survival potential and to address their stability at different time scales. We used biochars produced by gasification at temperatures > 1000°C and hydrochars produced by hydrothermal carbonization at temperatures of 230°C from maize silage. Moreover, we sampled pyrogenic C produced from recent forest fires as well as Holocene charcoal from forest fires as well as charcoal pits. Different types of pyrogenic C were subjected them to chemical oxidation, physical alterations and microbial decay during laboratory studies. Stable isotope tracing was used to determine specifically the amount of biochar released during laboratory incubations.

Our results showed a strong relationship between elemental composition and resistance to chemical oxidation (Fig. 1), suggesting that chemical oxidation may be used to characterise the degree of condensation of aromatic C.

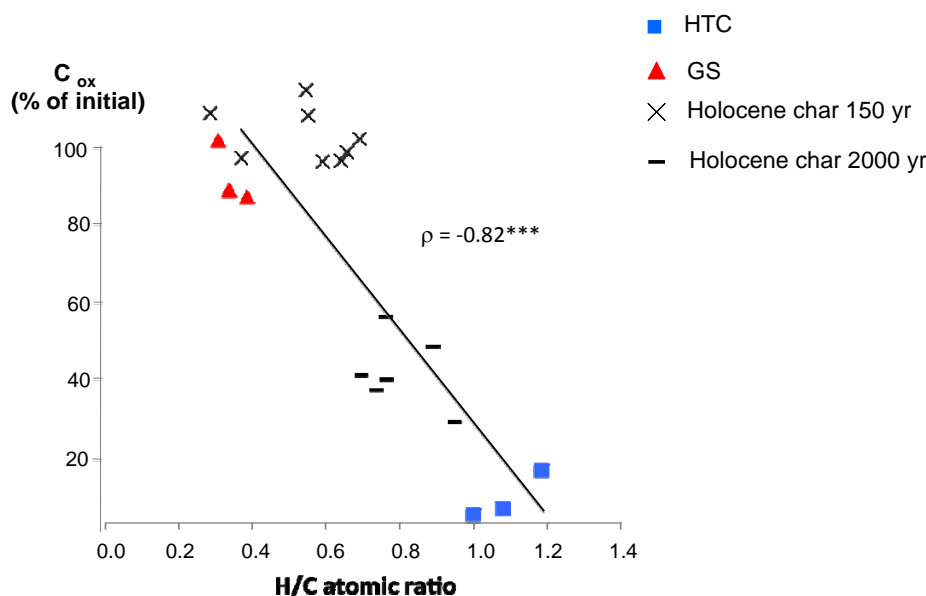


Figure 1. Relationship between oxidation resistant C and elemental composition for modern biochars (GS), hydrochars (HTC) and Holocene chars of different age (from Naisse et al., 2013)

The resistance of recent pyrogenic C to this method was dependent on its particle size, suggesting higher stability of bigger particles compared to smaller ones (Rumpel et al., 2007; Nocentini et al., 2010). Pyrogenic N was lost more rapidly than pyrogenic C leading to increased C:N ratios after oxidation. C:N was also increased for Holocene chars as compared to recent biochars and hydrochars, suggesting that N may be more labile under environmental condition than C. Reactivity of pyrogenic C seemed to decrease with increasing environmental exposure time as 2000 year old chars were more susceptible to chemical oxidation than 100 year old chars (Naisse et al., 2013).

We hypothesised that physical weathering may influence the survival potential of pyrogenic C in soil and subjected recent biochars and hydrochars to physical weathering. It was interesting to note that despite a greater chemical stability, gasification chars were more susceptible to physical weathering than hydrochars. Physical weathering increased the reactivity of gasification chars and had no effect on the chemical reactivity of hydrochars.

Biological stability of pyrogenic C was assessed during short-term incubations in soil. In general, biological stability of pyrogenic C was related to its elemental composition indicating its degree of condensation. Biological stability was not modified after physical weathering suggesting that physical weathering affects mainly the longterm survival potential of pyrogenic C.

We suggest, that a combination of methods is necessary to evaluate the potential mean residence time of pyrogenic C in soil.

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FATE OF BIOCHAR CARBON FROM CORN STOVER AFTER A 510 DAY- INCUBATION IN AN ANDISOL AND ALFISOL

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An incubation experiment was conducted (i) to investigate the evolution of CO₂ from soils amended with fresh corn stover or with biochar produced from corn stover at either 350 or 550 °C (CS-350 and CS-550) and incubated for 510 d, (ii) to evaluate the priming effect of these biochars on native organic matter (NOM) decomposition, and (iii) to elucidate the fate of biochar in physically- and chemically-defined fractions of organic carbon (OC). Two soil types were studied: a Typic Fragiaqualf (TK soil) and a Typic Hapludand (EG soil). Except for the controls, all treatments received 7.18 t C ha⁻¹ (5.6 and 6.3 g kg⁻¹, for the TK and EG soil, respectively). We measured total carbon (C) efflux and its isotopic signature to distinguish between C evolved from C₃ dominated native organic matter and C₄ dominated amendments. After 295 d, two undisturbed subsamples from each pot were taken: (i) in one subsample, lucerne (*Medicago sativa* L.) was seeded; (ii) in the other, the incubation was continued without plants. Soil samples at 0 (T0), 295 (T295) and 510 d (T510) were physically fractionated into coarse free particulate organic matter (fPOM), fine fPOM, silt+clay and heavy fractions, and analysed for $\delta^{13}\text{C}$ and total OC.

For a given soil, no significant differences ($P < 0.05$) were observed in the rate of CO₂ evolution between the controls and biochar treatments. Total accumulated CO₂ evolved from the uncharred corn stover treatment was significantly higher ($P < 0.05$) than that from the other treatments, with a loss of >65 % C of the material added. At the end of the incubation with uncharred corn stover, a net positive priming effect on decomposition (enhanced the rate of decomposition) of NOM was observed in the two soils. In the presence of biochar, a net negative priming effect on NOM decomposition was observed in the TK soil, but no clear net effect was detected in the EG soil. A C balance indicates that the C lost from both biochar production and decomposition “breaks even” with that lost from residue decomposition in less than 35 weeks (Fig. 1). The “break-even” point is reached earlier in the EG soil amended with the low-temperature biochar. When the different priming effects on NOM were considered in the C balance, the differences among the two soils disappeared.

After 295 d, $\delta^{13}\text{C}$ fractionation revealed that >74 % (TK soil) and >64% (EG soil) of the biochar-C was recovered in the coarse fPOM fraction; 13 – 18% (TK soil) and 21 – 30

% (EG soil) in the fine fPOM fraction, and minor amounts in the silt+clay fraction. The same pattern was observed after 510 d, both with and without plants, although a significant increase ($P<0.05$) in the recovery of biochar C in the silt+clay fraction was observed, especially in the presence of plants. Most of the biochar particles thus concentrated into the fPOM fraction, so-called “unprotected pool”, which is generally considered as “labile C”. Treatments including the presence of both biochar and plants induced an additional accumulation of OC in the TK-350 and EG-550 soils ($P<0.05$), compared with the treatments with plants but no biochar. A method to improve the physico-chemical fractionation of biochar-amended soils is proposed in this study. The use of long-term incubations in studies of soil OM turnover (including biochar) where no inputs of fresh detritus are made is discouraged.

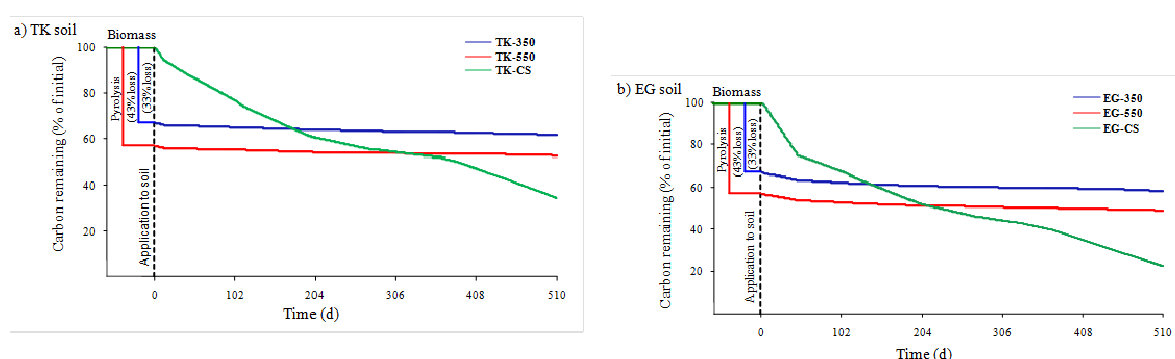


Figure 1. Carbon of biochar from corn stover produced at 350 °C and biochar produced at 550 °C that remains after pyrolysis and 510 d incubation in (a) a Tokomaru soil, and (b) an Egmont soil at a dose of 7.18 t C ha⁻¹. The C lost when the same amount of C was added as fresh corn stover (at the same dose) was also represented.

PYROGENIC C AS A SOURCE OF MOLECULAR PROXIES FOR SOIL C STABILIZATION MECHANISMS

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A review on the specific chemical characteristics of pyrogenic C, other than those found in biomacromolecules present in natural soil organic matter (SOM) is carried out. Special emphasis is paid to the possible meaning of these characteristics in the performance of the biogeochemical processes involved in soil C sequestration. In addition, a series of fire-induced effects modifying the composition, structure and properties of SOM leading to accumulation of resilient C-forms in soil are discussed from the results of field and laboratory studies.

According to our findings, the most outstanding generic effects of intense fires on humic-type SOM concern mainly to changes in its solubility and colloidal properties, reflected in quantitative changes in the relative amounts of the water-soluble fractions and fulvic acids (acid-and alkali-soluble SOM fractions), which turn into macromolecular substances similar to humic acids (acid-insoluble, alkali-soluble SOM fraction), which are further transformed into humin (insoluble SOM). Further heating leads to the progressive transformation of this humin into a recalcitrant, pyrogenic, black-carbon-type condensed residue not amenable to mild chemical degradations (Almendros and González-Vila, 2012).

From the structural viewpoint, intense heatings systematically lead to a simplification of the SOM composition, which is transformed into a C–C and C–O condensed matrix (in some cases having ca. 50% alkyl structures resistant to fire, with minor amount of nonhydrolyzable C=O groups), which is frequently compared to fossil protokerogens. Nevertheless, pyrogenic SOM forms in the intermediate stages of charring may show enhanced structural complexity as a consequence of the transformations of each of the original constituents into a plethora of derivatives after thermally-induced reactions (De la Rosa et al., 2012). The most classical example is the molecule of glucose, which after heating turn into more than 50 major compounds ranging from anhydrosugars (levoglucosenone, cyclic ketones) to furans and benzenic compounds.

The above effects often represent an increase in the chemical complexity and biogeochemical stability of the SOM, which are evidenced by laboratory incubation experiments. Heavily transformed pyrogenic SOM forms probably have increased resistance to degradation as a consequence of their high aromaticity and condensed macromolecular structure, whereas charred SOM in intermediate stages of formation of black carbon becomes increasingly resistant to degradation probably due to the thermal generation of compounds not existing in biomass, arranged into chaotic macromolecular structures not readily recognized by specific soil enzymes.

Apart from the above general behaviour, non-systematic fire effects depend on local environmental constraints and the wide differences in fires' intensity, fire's propagation patterns and soil moisture during the passage of the fire (Keeley et al., 2012). For this reason, laboratory simulation experiments are indispensable to differentiate fire intrinsic effects on the soil, from those produced by fire-induced inputs of charred necromass from the vegetation.

The structural changes paralleling the progressive transformation of colloidal (humic, fulvic-type) fraction into pyrogenic SOM forms are mainly decarboxylation, dehydration (increase in water repellence), demethoxylation of phenol compounds (progressive smoothing of the lignin signature), dealkylation (selective thermal degradation), cyclations (newly-formed aromatic rings mainly from O-alkyl compounds) and structural condensations (such as formation of melanoidins through carbohydrate dehydration) leading to condensed polycyclic structures (González-Pérez et al., 2004). Thermal formation of heterocyclic N-forms from SOM precursors exclusively consisting of acyclic amide forms has been confirmed both in heated biomass as in fossil humic-type substances (Almendros and González-Vila, 2012).

In the case of the particulate SOM (with comparatively low oxygen-containing surface functional groups and practically lacking of colloidal properties) the impact of fire is not recognized in the solubility properties, but mainly in the increased water repellence probably caused by rearrangement of the alkyl moiety of these SOM forms: in particular free (extractable) lipid typically decreased in amount as a consequence of fires' intrinsic effects, whereas SOM hydrophobicity increases (suggesting a weak influence of the accumulation of extractable lipids, but changes in surface properties and molecular composition).

The above thermal diagenetic patterns of the SOM could be justified by its transformations at a molecular level. In general alkyl compounds after fire show decreased chain length (in addition to even-to-odd carbon preference index close to the unity), are more diffusible into condensed SOM matrices (molecular encapsulation of thermal breakdown product or otherwise extractable, free lipid), or may also condense into new polyalkyl humic structural domains, as suggested by the protokerogen-like ¹³C-NMR patterns of charred SOM in intermediate formation stages of black carbon.

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CHEMICAL COMPOSITION AND BIOLOGICAL STABILITY OF PYROGENIC C FROM A NATURAL FIRE

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The work presented here is a synthesis of an article series conducted on natural charcoal in the environment (Alexis et al., 2007, Alexis et al. 2010, Alexis et al., 2012). The objective was to characterize the alteration of OM resulting from thermal alteration and to follow the fate of the produced pyrogenic C in soil.

This work was led in the oak scrub, located on the *Merritt Island Wildlife Refuge* in Florida. The climate is sub-tropical, the soil is a sand-dune *Entisol* (acidic and high drained). The ecosystem is managed by prescribed fire since the 50's, with fire return interval about 11 years. One of these fire events was especially studied with the quantification and characterization of organic matter (plant, soil and litter) before and after the fire. The maximum temperature reached during the fire was assessed using thermo-sensitive paints, placed in the vegetation and litter. From this measurement, the fire intensity was qualified as "moderate". Four plots protected from fire for 1, 4, 11 and 20 years was also identified as a chronosequence. Three soil depths were sampled: 0-5 cm, 5-15 cm and 15-25cm.

The fresh OM, the charcoal and the soil OM were analysed for C content and *Oxydation Resistant Elemental Carbon* (isolated through K₂Cr₂O₇/H₂SO₄ attack). The solid-state ¹³C NMR spectroscopy was also used to characterize the charcoal produced by fire and the SOM. The evolution of soil C stocks and OREC stocks after fire were assessed along the chronosequence.

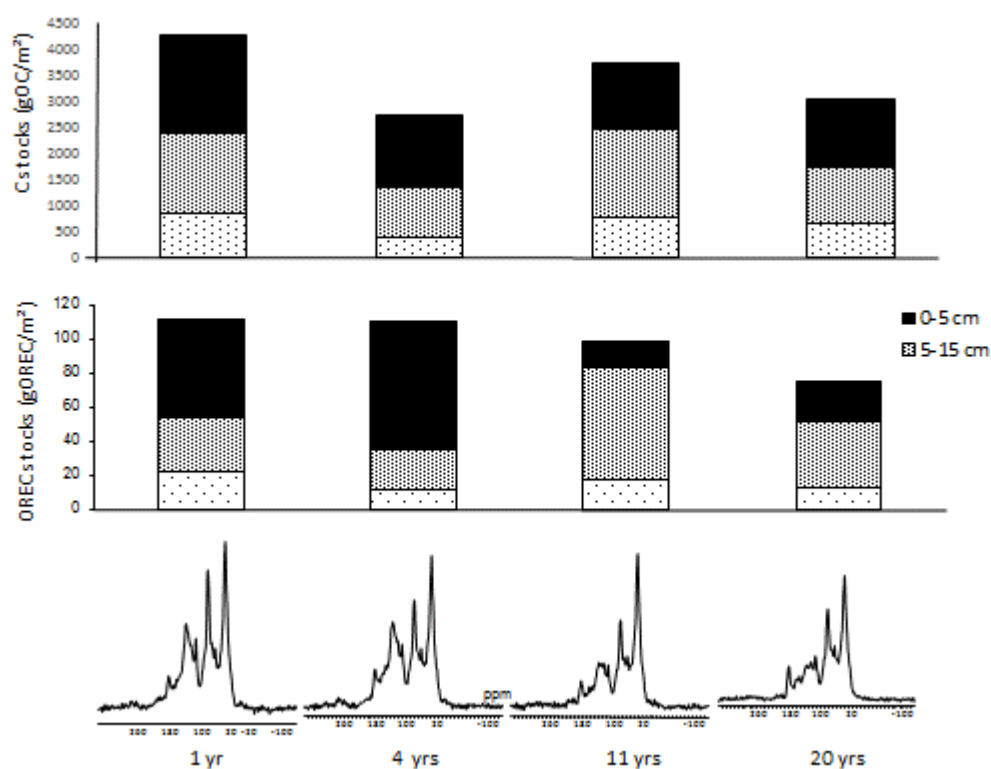
The thermal alteration led to an increase of C content in litter, which was 56, 59 and 59 % in <1 mm, 1-2 mm and >2 mm, respectively. This C concentration was related to an increase of aromatic C content of the OM that was 45, 50 and 50 % OC respectively in the latter size-fractions. The temperature reached during the fire appeared as a controlling factor of this aromatic C content of charcoal particles. In the 0-5-cm soil, the ¹³C NMR spectra showed a dilution of the charcoal signal in the non-pyrogenic soil organic matter (figure 1). Moreover the aromatic C proportion decreased along the chronosequence, especially between 4 and 11 years after fire.

The charcoal production through prescribed fire was about 140 mg C/m² and it represented about 3.4 % of pre-fire C stocks. The OREC content was about 4% OC in charred stem, and 16% in charred leaves. As a result, the OREC production through prescribed fire was about 15 g C/m². Along the chronosequence (figure 1), the soil C stocks decreased from 4.3 kg C/m² 1 year after fire to 3.0 kg C/ m² 20 years. The same trend was observed for the OREC stocks, which decrease from 112 g C/m² 1 year after fire to 75 g C/m² 20 years after fire. The distribution between soil depths also appeared modified with a transfer of C and OREC from 0-5 cm to 5-15 cm.

Comparing the input and soil stocks of OREC allowed concluding that, despite gradually accumulated with fire events (stocks are higher than input resulting from 1 fire), the "natural" pyrogenic material may be subjected to significant degradation in

soil. It is noteworthy that the OREC measured in this study, through harsh oxidation, may be an underestimation of the pyrogenic C fraction. It also mean that only the most recalcitrant part of pyrogenic C is observed and that the degradation rate may be overestimated. These conclusions are probably the consequence of the soil and climate characteristics of the study site that both enhance the soil organic matter degradation.

Figure 1. 1st part: Evolution of C stocks for the 0-5 cm, 5-15 cm, 15-25 cm along the



chronosequence. 2nd part: Evolution of OREC stocks for the 0-5 cm, 5-15 cm, 15-25 cm along the chronosequence. 3rd part: ¹³C NMR spectra obtained for the OM collected at the 0-5 cm depth 1 year, 4 years, 11 years and 20 years after the fire.

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ORAL PRESENTATIONS

Session 2. Characterisation of pyrogenic C forms

WHAT IS THE DIFFERENCE BETWEEN PYROGENIC CARBON OF NATURAL AND ARTIFICIAL SOURCES? A CASE STUDY FROM A PINE FOREST FIRE

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The environmental recalcitrance of Pyrogenic Carbon (PyC), both produced in vegetation fires (charcoal), and man-made (biochar), gives it the potential to act as a medium/long term sink of atmospheric carbon. Sustainable production of biochar and its addition to soils is currently debated as one of the most viable global approaches for carbon sequestration and climate change mitigation (Woolf et al. 2010). Also the role of its 'natural counterpart', i.e. wildfire charcoal, as a long-term carbon pool in soils is recognized within the PyC research community (Lehmann et al. 2008).

In spite of their fundamental similarities, research on the potential of 'man-made' biochar and wildfire charcoal for carbon sequestration has to date been carried out essentially in isolation. In this presentation we will compare, for the first time, characteristics of man-made biochar and wildfire charcoal generated from the same material under known production conditions: charcoal generated in the forest floor of a pine forest (*Pinus banksiana*) during an experimental wildfire with monitored burn temperature/duration vs. biochar produced from the same feedstock under three pyrolysis conditions [2h at 350, 500 and 650°C].

Biochar and charcoal samples are being characterised for: i) elemental composition (elemental analyses and isotopic signature); ii) thermal recalcitrance (Differential Scanning Calorimetry; DSC); iii) composition of functional organic groups (Fourier Transform Infrared spectroscopy) and iv) surface area and morphology (Scanning Electron Microscopy).

Some preliminary results are shown in Table 1. They indicate a high variability among the different types of PyC characterised. The wildfire charcoal does not only differ to the man-made biochar, but also the biochar characteristics vary depending on the production temperature.

Table 1. Characteristics of the original material (feedstock) and charcoal and biochar derived from it.

	Conversion (% original weight)	C (%)	N (%)	C/N	$\delta^{13}\text{C}$ (‰)
Feedstock		40.5	1.0	39.6	-28.1
Wildfire					
Charcoal	30	54.7	1.3	44.7	-29.0
Biochar 350 °C	62	58.3	1.7	33.5	-29.4
Biochar 500 °C	46	64.6	1.8	35.0	-29.2
Biochar 650 °C	40	64.3	1.3	49.3	-29.3

Maximum production temperature was highest for wildfire charcoal (avg. 750°C, ranging from 550 to 976°C); however, the DSC analyses performed to date (Fig. 1) suggest higher thermal recalcitrance for biochar, specifically for that produced at 650°C, which may be related to other formation factors such as oxygen availability and/or charring time.

Further results on the similarities and differences between man-made biochar and wildfire charcoal will be presented and the implications of our findings will be discussed in the context of knowledge transferability of pyrogenic carbon characteristics between the biochar and the wildfire research communities.

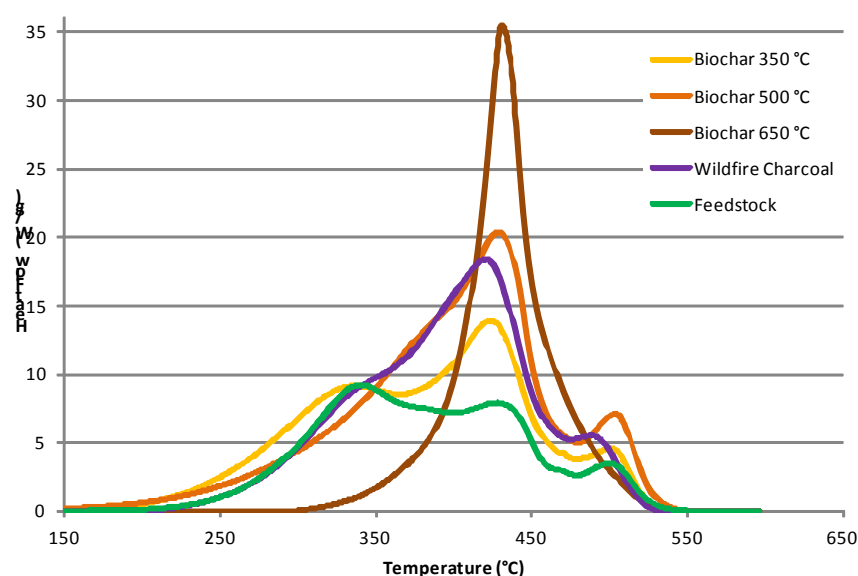


Figure 1. Differential Scanning Calorimetry thermograms for the original material (feedstock), wildfire charcoal and biochars.

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PYOM CHARACTERISATION IN FIRE-PRONE MEDITERRANEAN PINE FORESTS

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Fire is a major disturbance to vegetation and soil and a driving factor of ecosystems in the Mediterranean basin, as up to 90% of all forest fires in the EU occur in Mediterranean countries (De la Rosa et al., 2008). The aboveground vegetation and the soil organic matter (SOM), which is the fuel in soil, are affected in terms of both abundance and composition. Fire impact on soil organic matter is usually confined to the organic horizon and a few top cm of the underlying mineral soil (Certini et al., 2011). A major outcome of wildfires is the production of charcoal – the result of incomplete combustion of plant biomass and litter - and its release to soil (Knicker, 2011). In terms of composition, fire increases the heterogeneity of soil organic matter (SOM) because apparently no original component is totally removed, while new thermally-condensed aromatic compounds form as a consequence of chemical reactions driven by the high temperatures (González-Pérez et al., 2004). These fire-derived compounds collectively form the so-called pyrogenic organic matter (PyOM). Some PyOM is usually reported to have longer residence times in soil compared to the parent materials, enhancing the potential of soil to store carbon for long time, offsetting the release of human induced CO₂ to the atmosphere (Schmidt and Noack, 2000). However, PyOM structure and composition is not yet well-understood. PyOM is not so inert as formerly believed (Farrell et al., 2013) and can play crucial roles in soil biological processes (Zackrisson et al., 1996) and on SOM dynamics (Wardle et al., 2008). Consequently, there is gathering interest in collecting reliable information on structure and properties of PyOM and understanding its behaviour in soil. Mediterranean soils, in spite of being particularly affected by wildfires, were poorly investigated compared to soils of other environments.

The present work deals with some wildfires occurred in Mediterranean pine forests of Tuscany, central Italy, and it is aimed at disentangling the composition and structure of PyOM produced during wildfire. To overcome the complexity of the investigated matter, we used various techniques and we fractionated charcoal according to particles size, starting from the assumption that those fractions have different composition and reactivity, which is plausible on the basis of previous studies (Rumpel et al., 2007; Nocentini et al., 2010; Francioso et al., 2011).

By thermal (thermogravimetry, differential scanning calorimetry) and spectroscopic (FT-IR, Raman, NMR) techniques, we observed that fire caused an accumulation of recalcitrant and refractory compounds at the expense of the SOM

fraction most labile to thermal degradation. Charring, on the other hand, was not complete, as part of the burnt material still contained a fraction thermally degradable under 500 °C. As a consequence, the partly charred materials accumulated on the surface and into the first layer of mineral soil are prone to be oxidised by further fire events. The thermally recalcitrant pool was enriched in N polyaromatic molecules whose formation provides evidence that PyOM formed at temperatures not exceeding 400 °C.

The size fractions we separated the macroscopic charcoal, actually showed different elemental composition, lignin signature and reactivity, as verified by dichromate chemical oxidation. This induces to hypothesise different precursor plant materials from which these fractions were originated and/or different fire conditions under which they were produced. Spectroscopic analyses (FT-IR, normal Raman, surface-enhanced fluorescence and surface-enhanced Raman scattering, NMR) support such a hypothesis, clearly showing that the charcoal found on the ground immediately after a wildfire has a different chemical structure depending on size of particles, type of burnt biomass and fire conditions under which charcoal was produced. In particular, fine charcoal is generally less aromatic but richer in N-bearing aromatic structures, aliphatic chains and carbonyl groups; it is also more reactive, suggesting a relatively fast mineralisation in soil. On the contrary, the coarse fractions are less reactive, mainly comprising condensed aromatic material apparently more crystallised, being probably composed of larger graphitic clusters.

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BIOCHAR SURFACE PROPERTIES THROUGH APPLICATION OF AN INNOVATIVE NMR TECHNIQUE: FAST FIELD CYCLING RELAXOMETRY

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Biochar is a carbonaceous material obtained by pyrolysis of biomass feedstocks. It is applied to soils in order to improve fertility and mitigate greenhouse-gases emissions. In fact, from the one hand, biochar changes physical-chemical soil properties, thereby affecting soil fertility. From the other hand, biochar is resistant to chemical and biochemical degradation. For this reason, its use allows carbon sequestration in soils and consequent reduction of carbon dioxide to the atmosphere.

Here, dynamics of water at the liquid-solid interface of water saturated biochars is discussed. Results revealed that water dynamics is affected by the nature of biochar parent biomasses. Moreover, biochar chemical physical properties are affected by conditions for their production.

It was understood that water undergoes to an inner-sphere interaction mechanism with biochar surface through formation of weak unconventional hydrogen bonds.

Recognition of the interaction mechanisms between water and biochar is of paramount importance in order to understand why biochar soil amendments improve soil fertility and crop production.

ORAL PRESENTATIONS

Session 3. Effects of pyrogenic C on soil organic matter

CHARCOAL – A SOIL FORMING FACTOR IN FREQUENTLY BURNT SOILS?

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Natural and prescribed vegetation fires lead to the input of considerable amounts of charcoal into soils. This amount will even increase by the application of biochar as a tool for improving soil fertility. It is well accepted that an immediate effect of charcoal input represents the enhancement of the aromaticity of the soil organic matter (SOM) in particular of the topsoils. However, our knowledge about the long-term impact of this material on SOM and on general soil properties is still scarce. In order to fill this gap, several soils with expected and known fire-history were characterized by solid-state nuclear magnetic resonance (NMR) spectroscopy. Their respective pyrogenic organic matter (PyOM) content was elucidated after their chemical oxidation with acid potassium dichromate and the quantification of chemical oxidation resistant aromatic carbon (CORECarom).

The first sample set comprised three profiles (Humaquepts) derived from the protected region of the Doñana National Park, which is located at the mouth of the river Guadalquivir in Southern Spain and represents one of the largest marshlands reserves of Europe. Although fires are now prevented as far as possible, some of the areas were formerly subjected to frequent prescribed fires since 1628. Two of the selected profiles had experienced no fire since installation of the park in 1969. Here, no major quantities of PyOM were recovered in the O layer, but an increase of aromaticity correlating with PyOM contents was revealed with soil depth. At both sites, PyOM accounted for more than 15% of the C_{tot} in the A/C horizon (> 50 cm). This clearly evidences a downward translocation of charcoal within the soil profile. The third profile derived from a site which suffered a severe fire in 1985. The fire combusted the entire O layer (0-20 cm), but after 19 years, the latter recovered to approximately 15 cm, although only minor contributions of PyOM were revealed. Whereas directly after the fire, the soil at a depths of 55 cm contained only 3 mg g⁻¹ organic C without any evidence of PyOM, after 16 and 19 years a clear increase of C_{tot} (10-15 mg g⁻¹) with a considerable contribution of PyOM (12% of C_{tot}) was revealed. Although the absolute concentration of PyOM did not decrease in the lower depths, its relative contribution to C_{tot} declined. This may be explained by the constant input of fresh litter, which on a long term masks the presence of char. Alternatively, an efficient downwards transport within the sandy profile and subsequent stabilization of PyOM may have occurred. A comparable feature was observed for Ferralsols derived from the Cerrado in Central Brazil.

The second sample set derived from “Tierras negras andaluzas” which are Vertisols occurring frequently in the valley of the Guadalquivir. Being fertile, they have been cultivated since millennia. Analysis of their SOM by solid-state ¹³C NMR spectroscopy revealed high contents of aromatic C (up to 35% of the total organic C).

Preliminary ^{14}C dating indicated a mean age of the SOM of approximately 5000 years. Chemical oxidation with acid potassium dichromate confirmed considerable contributions of PyOM which may have been introduced into the soils as a consequence of early slash and burn. A further source represents continuing after-harvest-burning of crop residues, which since ancient times was and occasionally still is a common agricultural practice in this area. In contrast to the soils of the first sample set, high PyOM contribution to the total SOM were evidenced even in the topsoil, which may be best explained a selective preservation of charcoal supported by scarce fresh litter input due to crop removal and burning of the remains.

In summary, the studied profiles clearly indicate that charcoal input alters the chemical composition of SOM on a long-term scale. Whereas in the agriculturally used Vertisols with their low input of fresh litter, this is clearly expressed by a high aromaticity of the SOM of both sub and topsoil, in soils with frequent input of fresh litter the alteration of SOM composition is mainly manifested in the subsoils. Our results demonstrate further that limiting the quantification and characterization of charcoal to the upper horizons is likely to result in its underestimation. With respect to modern agriculture, the possible transport and stabilization of PyOM residues has also to be considered if one intends to elucidate the sustainability of artificially produced biochars as possible soil amendments.

WILD-FIRE INDUCED CHANGES IN THE QUANTITY AND QUALITY OF ORGANIC MATTER ASSOCIATED TO THE MINERAL PHASE

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In Mediterranean ecosystems, wildfires occur frequently and lead to formation of Pyrogenic organic matter (PyOM). After fire events, such material is quickly incorporated into the soil and causes changes of the quantity and quality of soil organic matter (SOM). The charring process involves chemical alterations of the litter material, which are manifested in the transfer of biologically available structures such as carbohydrates, proteins and lipids into aromatic polymers.

In fire affected soils (FA), PyOM is expected to alter the N-bioavailability and thus the N-competition and the N-partitioning between plants, soil (micro) organisms and sequestration of nitrogen (N) into SOM. At the same time PyOM is considered a major N protection mechanism. However, recent studies indicated that N incorporated into PyOM can be used for plant growth.

Whereas an impact of charcoal on the soil organic carbon (SOC) pool is well recognized, the effect of fire on the soil organic nitrogen (SON) is often neglected. In the present study, we combined routine and advanced solid-state ¹³C and ¹⁵N NMR spectroscopy with wet chemical analysis to characterize the organic N in the density and particle size fractions of fire-affected soils from the Sierra de Aznalcóllar, Southern Spain.

First results confirmed that both, the quality and quantity of N are affected in all particle size fractions. Some studies revealed the formation of carboxylic groups during the microbial transformation of charcoal. Such groups can increase the solubility of charred residues in the soil solution but can also interact strongly with the mineral phase.

Respiration experiments indicated that in our soils charcoal is biochemically less recalcitrant than commonly assumed. The mean residence times of the charcoal fraction in fire-affected soils were only slightly longer than those observed for fire unaffected (FU) organic material.

Elemental analysis of the organic material of the bulk soils indicated an enrichment of organic C and N caused by the fire event. Comparison of the chemical composition of the charred and fire unaffected plant residues confirmed that wild fires lead to a considerable increase of aromatic structures and a decrease of O-alkyl and peptide components.

Examining the composition of organic matter associated with the different particle size separates of the FU soils by solid-state ^{13}C NMR spectroscopy, confirmed this pattern.

Accordingly, the solid-state ^{15}N NMR spectra of the fire affected soils revealed the presence of pyrrole-type compounds. The contribution of those to the total organic N was highest in the sand-size fraction. However with increasing time after the fire event, the charcoal pattern turns less pronounced possibly due to ongoing degradation processes. This is likely to be supported by the continuous input of fresh litter leading to a recovery of the dominance of fire- unaffected SOM.

CAN N-RICH CHARCOAL BE USED AS AN EFFICIENT N FERTILIZER?

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After wild fires, considerable amounts of charred vegetation residues can be incorporated into the soil. They derive from incomplete combustion and contribute to the pyrogenic organic matter (PyOM) or as it is also referred to as “Black Carbon” pool of soils.

However, since depending on the source material, this material can contain a considerable amount of organic nitrogen as an integral part of PyOM, the ecological role of the so called “Black nitrogen” (BN) should not remain unobserved. Most of Mediterranean soils are poor in organic matter (OM) and have also low nutrient bioavailability.

In order to obtain a better understanding of the impact of charcoal on the nitrogen (N) cycling in soil, ^{15}N enriched pyrogenic organic material (PyOM) obtained from “*Lolium perenne*” charred for 4 minutes at 350°C was mixed with a typical Mediterranean agricultural soil (*calcareous Rhodoxeralf*) and incubated for 72 days under controlled conditions.

The main objectives were to analyse the availability of N from this material and to obtain more insight into the recalcitrance of PyOM in soils. Addition of artificially produced ^{15}N -PyOM increased the biomass production and N retention. After 72 days of incubation time, 10% of the ^{15}N added to the soil ($^{15}\text{N}_{\text{add}}$) was incorporated into new grass biomass.

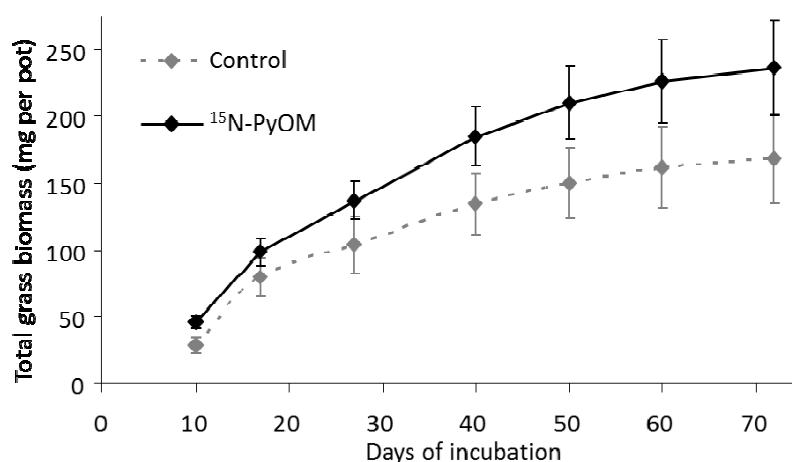


Figure 1. Aboveground biomass production of *Lolium perenne* grown on with and without addition of ^{15}N -enriched PyOM. Biomass values are given per pot.

Solid-state ^{15}N NMR spectroscopy revealed that at least some of this N derived from the degradation of pyrrole-type structures. Increase of the amide-N intensity in the solid-state ^{15}N NMR spectrum of the incubated soils indicated further that some ^{15}N from the PyOM was also incorporated into new microbial biomass.

Considering that BN components represent a large part of the organic C in grass chars, their fast degradation implies that such material may not as recalcitrant during long-term humification as formerly thought, which is in agreement with recent studies revealing relatively short mean residence times of less than 100 years (Hamer et al., 2004; De la Rosa and Knicker, 2011). Although we are aware that the optimized laboratory conditions and the use of finely pulverized PyOM promoted a much faster degradation than expected in natural soil systems, the relatively fast but controlled availability of N from N-rich PyOM suggests a relatively low recalcitrance of N-rich PyOM. Since during its degradation, N is only slowly transferred into a plant-available form, it may contribute to the observed improvement of soil fertility by avoiding fast N-losses due to leaching and volatilization as a slow N-release fertilizer.

Therefore, with the present study we were able to demonstrate for the first time that in fire affected soils, the N used for the build-up of new plant material can also derive from the mobilization of organic N previously bound in PyOM. Consequently, N-rich PyOM operates as an organic N-fertilizer.

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OBSERVATIONS ON WILDFIRE BLACK CARBON IN SHALLOW SOILS OF THE NORTHERN ALPS

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The stability and storage of wildfire-derived black carbon (BC) in soils is important for regional and global carbon balances. In the study area in the Northern Limestone Alps (Austria), wildfires are rare; mean fire intervals (MFI) range from 200-500 yrs to several millenia. However, fires may be stand-replacing and can trigger severe erosion and vegetation destruction with the possibility of secondary natural hazards like rockfall, debris flows and avalanches. The aim of our study was to find out if, where, and to which extent charcoal is stored in the Rendzic Leptosols of the affected slopes and if the charcoal can be used to reconstruct the location and the extent of earlier wildfires. We wanted to find out if the BC produced by wildfires modifies with time (by weathering or decomposition) and if there is a concentration of BC at certain depths or in certain soil horizons, which might in turn provide evidence of the elapsed time since the fire.

We took soil samples from shallow soil pits on approx. 20 sites in the Tyrolean Limestone Alps, screened them in the field and in the lab for macroscopically visible charcoal fragments (> 1mm) and tried to derive a simplified model of spatial distribution and temporal behaviour. Several BC fragments of unknown age were ¹⁴C-dated. In a second, more detailed approach, we investigated soil samples of four burnt slopes with varying age after fire (wildfires occurred in 2003, 1962, 1946 and 1250 AD) as well as of the surrounding soil that was not affected by combustion. Charcoal content of O and A horizon was determined as well as pH, soil organic matter content and C/N ratios.

The results show that significantly elevated BC concentrations can be found on known historical wildfire sites, even if there is a certain ubiquitous background concentration which is probably due to aeolian transport and to earlier fires. The position of BC fragments within the soil profiles is influenced by fire characteristics and by the intensity of erosion; with vegetation and soil recovery, zones of maximum charcoal accumulation shift further downwards in the soil profile. Charcoal concentration and mean BC particle size decrease with age due to erosion and translocation; however, if erosion is moderate, charcoal can be conserved for centuries. A conceptual model was developed which shows where BC can probably be found in the profile considering fire intensity, erosion and translocation.

Soil organic matter contents significantly decreased on burnt slopes, which is due to vegetation combustion, long-term vegetation changes and intensified erosion. However, in the long-term re-accumulation occurs due to the recovery of vegetation. Simultaneously, soil pH increases by combustion and is further modified by an altered

vegetation composition. C/N ratios remained widely stable with the soil N content reacting more sensitive to combustion. The results demonstrate that Alpine soils react sensitively on wildfires mainly because of the high slope angle, which causes not only short-term, but also long-term modification of vegetation composition and erosion.

ORAL PRESENTATIONS

Session 4. Charcoal in archaeology

CHARCOAL IN ARCHAEOLOGICAL RESEARCH – WHY PRESERVATION MATTERS

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Macroscopic charcoal is commonly used to reconstruct past environmental conditions, the vegetation and fire history. It is also used in archaeological research for radiocarbon dating and building chronologies of past events. The materials in the pyrogenic carbon continuum have different properties which depend on their degree of aromaticity and the charring conditions. Their properties influence also their resistance against decomposition once they are stored in soils or sediments. Under optimal conditions, charcoal can be stable in soils over millennia.

Charcoal or pyrogenic carbon in topsoils can have different sources. If soil charcoal should be used as a proxy for past fire events, it is necessary to investigate buried soils or sediments, e.g. colluvia, and to radiocarbon-date the samples. A large fraction of charred organic matter is microscopic charcoal and therefore not available for standard ¹⁴C-dating procedures. Compound-specific ¹⁴C-dating of chemically separated organic or charcoal fractions is possible but problematic (e.g., mixture of different sources, missing archaeological context) and rarely applied, especially for archaeological research questions. We found that charred organic matter isolated from soil material by UV-oxidation yielded ¹⁴C ages that were not comparable to ages from single macrocharcoal particles taken from the same soil samples (Eckmeier et al., 2009).

In terrestrial archives, several diagenetic processes affect charcoal preservation. If charcoal is missing in archaeological or environmental records, it should be investigated if the charcoal has always been absent, or if it was removed from the site by degradation or erosion. It was shown that older charcoal is prone to chemical decomposition (e.g. Cohen-Ofri et al., 2006, Braadbaart et al. 2009). Charcoal preservation in soils or sediments is therefore affected by a variety of natural, but also anthropogenic factors, which needs to be considered when reconstructing past fire events.

An example is the poor preservation of charcoal in prehistoric sites from the Natufian period (15-11.5 kyr BP) in the Southern Levant. Here, we investigated possible environmental factors that influenced the preservation of material for radiocarbon dating from the Natufian site of el-Wad Terrace (Israel). We analysed sediment samples, and selected charcoal for ¹⁴C dating using FTIR in order to gain information about the state of preservation of the samples. In average, about two-thirds of the charcoal mass was lost during the standard Acid-Base-Acid pretreatment, which is an indicator for poor structural condition of charcoal. A better recovery after final HCl was reached using a modified procedure after Rebollo et al. (2008) which omits the first HCl step. The poor preservation of charcoal could be attributed to the calcite compounds and the alkaline pH of the sediments (Eckmeier et al., 2012). A further question might be if the lack of macrocharcoal in man-made dark soils in NW Germany (Gerlach et al., 2012) which do contain pyrogenic carbon (measured as BPCA) might be a result of former alkaline conditions of the loess material in which they developed.

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ORAL PRESENTATIONS

***Session 5. Biochar: Production and characteristics.
Risks and benefits of its application to soils***

INFLUENCING BIOCHAR CHARACTERISTICS THROUGH PYROLYSIS CONDITIONS, FEEDSTOCK BLENDING AND POST-PRODUCTION TREATMENT

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Biochar is a highly complex and heterogeneous composite material. Its chemical and physical properties vary enormously. Besides the biomass feedstock composition, the pyrolysis temperature curve, the residence time in the pyrolysis chamber, the pressure and gas flow in the chamber and particularly the cooling regime of the dissipated educts have a major influence on the properties of a biochar. Consequently, the aromatic carbon content which is considered the “true core of biochar” range only between 15 and 40 weight % (Schimmelpfennig and Glaser, 2012), whereas thousands of volatile and semi volatile organic compounds (VOC) and labile organic molecules (LOM), which were mostly neglected as impure by-products, range from 15 to 55 wt.% (Spokas et al, 2011; Crombie et al, 2013). Biochar VOC and LOM are the least investigated and most varying constituents of biochar, although they play a major role for plant growth, soil biota and the interaction with the soil matrix (Graber et al, 2012; 2013).

An extremely important and so far also often neglected non-aromatic constituent of biochar is its mineral matter. This can range from less than 5 wt.% in wood-derived biochars to more than 10wt.% in biochars produced from crop residues and manure (Stephen et al, 2013). Mineral matter exists as separate micro and nano phases within the carbon lattice, acting as a conductor, semi-conductor or insulator (Stephen et al, 2013) and influencing the redox potential of the biochar and thus the interaction between roots, soil biota and mineral nutrient uptake. Certain minerals such as Fe and Mn induce even magnetic or paramagnetic hotspots within the carbon lattice (Safarik et al, 2012) or create cation bridges affecting the sorption capacity of the biochar. The degree of mineral-carbon-complexes within the biochar can be adjusted by blending the biomass feedstock with clay minerals, as it happens naturally in a forest or steppe fire where organic matter smoulders without oxygen on top and within the first few centimetres of the soil.

Using modern pyrolysis techniques, biochar-mineral-complexes with varying VOC content can now be produced under highly controllable process parameters. Based on these new experimental possibilities, new models on how biochar-mineral-complexes were and are produced in natural forest and steppe fires and how to predict their behaviour in the natural environment might be created. Moreover, first trials with the addition of clay minerals to the biomass feedstock have resulted in biochar-complexes with high fertilizing potential (Stephen et al, 2013), providing a new perspective for the use of biochar in soil amendment and as a nutrient carrier.

As the application of pure, untreated biochar to temperate soils seems not to lead to any substantial increase in soil fertility or plant growth (Jeffery et al, 2011) and as the

application of 10 tonnes or more of biochar per hectare is not economically viable for most farms, new methods of using biochar in farm settings need to be developed with a view to improving soil fertility and increasing soil organic matter, nutrient efficiency and ecosystem services.

To enhance the agronomic effects of biochar several post production treatments might be considered: (1) adding nutrients, (2) inoculating it with beneficial microorganisms, (3) improving its surface reactivity and porous volume and thus its sorption dynamics through traditional activation techniques, and/or (4) accelerated biological aging through composting or fermentation. The different post-production techniques can be classified according to the resulting physical and chemical alteration of the biochar:

1. Addition of nutrients, microorganisms and/or minerals in liquid solution which soak into the biochar pores without any or with only slight chemical alteration of the biochar.
2. Physicochemical activation (treatment with acids, vapours, toasting with minerals...), resulting in alterations of the surface, pore volume and functional groups.
3. Biochemical interaction of the biochar with organic compounds, minerals and microorganisms resulting in complexation of the aromatic structure and also partial degradation.

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THE JANUS FACE OF PYROGENIC CARBON REGARDING THE DISTRIBUTION AND AVAILABILITY OF ORGANIC POLLUTANTS

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Natural or anthropogenic pyrogenic carbon plays an important, but maybe ambivalent role for the fate and behaviour of organic pollutants in the environment. On the one hand, it acts as a strong sorbent for many organic contaminants (e.g., Cornelissen et al. 2005, Koelmans et al. 2006), on the other hand, it may contain such pollutants itself (e.g., Hilber et al. 2012). In any case, it greatly influences the distribution, bioavailability and bioaccessibility of these chemicals (Figure 1).

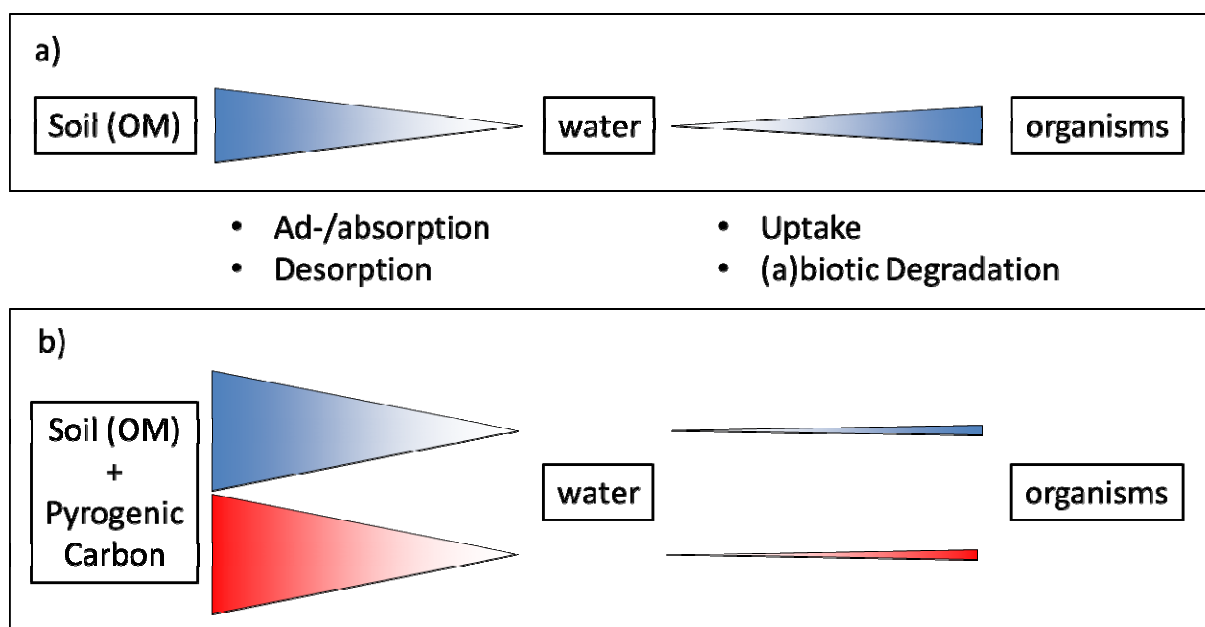


Figure 1. Distribution of many organic pollutants in the (terrestrial) environment and some relevant processes (bullets). Due to their hydrophobicity, pollutants will distribute predominantly into the organic matter fraction of soils, and organisms (a, blue triangles). Addition of pyrogenic carbon will pull them even more into soils (b, blue triangles), and thereby reduce exposures. Pollutants co-produced with pyrogenic carbon, such as PAHs (b, red triangles), are expected to largely remain sorbed.

In this contribution, examples to illustrate these manifold aspects of pyrogenic carbon will be presented. In particular, we will address total concentrations and bioavailable fractions of PAHs in biochar and possible measures to minimize them during or after production (Bucheli et al. 2013). We will further elaborate on how different forms of pyrogenic carbon have been used for remediation of polluted soils or sediments, and highlight the potential and limitations of this approach (Hilber & Bucheli 2010, Ghosh et al. 2011, Rakowska et al. 2012).

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POTENTIAL AND CONSTRAINTS OF BIOCHAR FOR PLANT-AVAILABLE WATER SUPPLY

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Biochar has a porous physical structure, which can absorb and retain water although its chemical structure is dominated by condensed aromatic moieties suggesting hydrophobicity. In addition, the pore size distribution of most biochars is dominated by pore diameters of $< 0.2 \mu\text{m}$ bind water with high capillary forces so that this water must be considered inaccessible for plants (Table 1). On the other hand, obtained results from real measurements strongly suggest positive effect of biochar for plant-available water supply.

Major et al. (2010) suggested that due to the physical characteristics of biochar, there will be changes in soil pore-size distribution and this could alter percolation patterns, residence time and flow paths of the soil solution. The water retention of Terra Preta was 18% higher compared to adjacent soils (Glaser et al. 2002). 20 Mg ha^{-1} biochar addition to a sandy soil in NE Germany increased plant-available water storage capacity by 100% (Liu et al. 2012). In a field trial in NE Germany, $5 - 20 \text{ Mg ha}^{-1}$ biochar application together with 30 Mg ha^{-1} compost significantly increased plant-available water both not only during wet but also during dry conditions when compared to the pure compost treatment or the control site, which did not receive any organic amendment (Fig. 1). This result was quite surprising as it was expected that the fine pores of biochar would retain water, which was not plant-available, which obviously was not the case. Therefore, biochar can indeed increase plant-available water supply. However, underlying mechanisms are not clear and theoretical contradictions need further attention.

Table 1. Connection of pore diameter, soil matric potential and plant-availability of soil water.

Matric potential [pF]	Soil suction [bar]	Pore diameter [μm]	Interaction processes	Plant-available
> 4.2	3.62	< 0.2	Adsorption, capillary forces	No
2.5	3.40	10	Adsorption, capillary forces	Yes
1.8	3.26	50	Slow movement	Yes
< 1.8	3.26	> 50	Fast movement	No

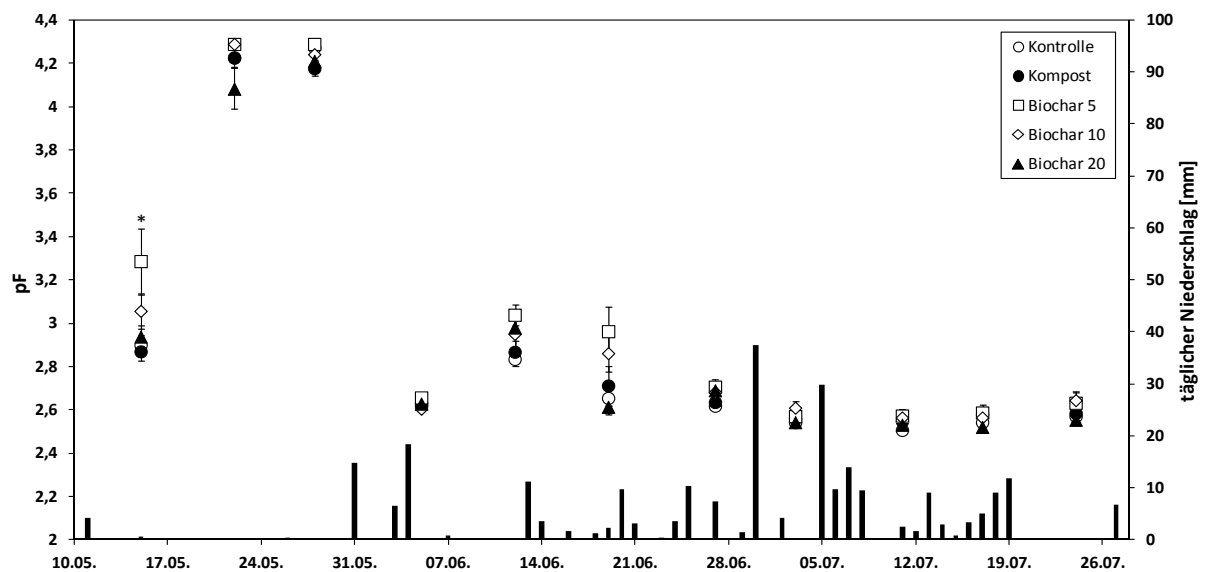


Figure 1. Soil matric potential (pF) in 10 cm (top) and 30 cm soil depth (bottom) in a sandy soil in NE Germany to which 30 Mg ha⁻¹ compost and 5 – 20 Mg ha⁻¹ biochar were added. Please note that water is available to plants between pF 2 – 4.2 and that water is not available to plants above pF 4.2. (from Bromm 2012).

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BIOCHAR AND SOIL HYDROLOGY UNDER MEDITERRANEAN CONDITIONS

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Biochar research is in its relative infancy and much more data are required to allow robust predictions of the effects of biochar application to soils. The research on the production-enhancing effect of biochar has largely focused on nutrient retention (cation exchange capacity; CEC), whilst the effect on water retention has received remarkably little attention after Tryon (1948). This also includes indirect hydrological effects, in particular that of reducing overland flow generation and associated soil, nutrient and carbon losses due to enhanced infiltration. Biochar's effect of enhancing infiltration would be especially relevant in drylands, where water availability is the principal limiting factor in agricultural production. At present, almost half of the Earth's land surface can be classified as dryland (UNEP, 1992), and this is expected to increase substantially under likely climate change scenarios. Viticulture in the Iberian Peninsula is reported to be particularly sensitive to the risk of increased drought (Schulz, 2000; Malheiro et al., 2010).

Will biochar reduce the soil's albedo and increase soil temperatures? Can biochar increase the transit time of water in dryland ecosystems? Do methods for measuring soil water content and soil water potential need to be modified? Is there enough biomass in drylands? Will biochar increase the risk of soil salinization? In this presentation we will set out the potential mechanisms by which biochar could contribute to soil hydrology related ecosystem services in Mediterranean environments, and discuss the potential pitfalls. We will then review the available evidence specific to effects of biochar on plant-available soil moisture content in different soils.

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POSTER PRESENTATIONS

THE EFFECT OF HEAT IN SOIL ORGANIC MATTER (SOM). EXPERIENCE FROM CONTROLLED BURNING EXPERIMENTS OF UNALTERED SOIL BLOCKS

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Wildfire is an important disturbance factor in many ecosystems, especially in the Mediterranean Basin (Keeley et al., 2012). Forest fires exert changes in soil organic matter (SOM) quality and quantity (González-Pérez et al., 2004) that in turn affect relevant and closely related characteristics like soil runoff and erosion response, due to changes on factors like wettability and aggregation (Certini et al., 2011; Mataix-Solera et al., 2011). The effects of heat in SOM are highly variable and dependent of many interrelated factors (Badía et al., 2011). Therefore SOM content may be affected from an almost total destruction to increases as a consequence of external inputs, mainly from forest necromass. Additionally to C losses or exogenous increases, pre-existing C forms in the soil may be transformed into recalcitrant pyrogenic material as black carbon (De la Rosa et al., 2012) contributing to the long term C and N sequestration in soils (Knicker, 2007; González-Pérez et al., 2008).

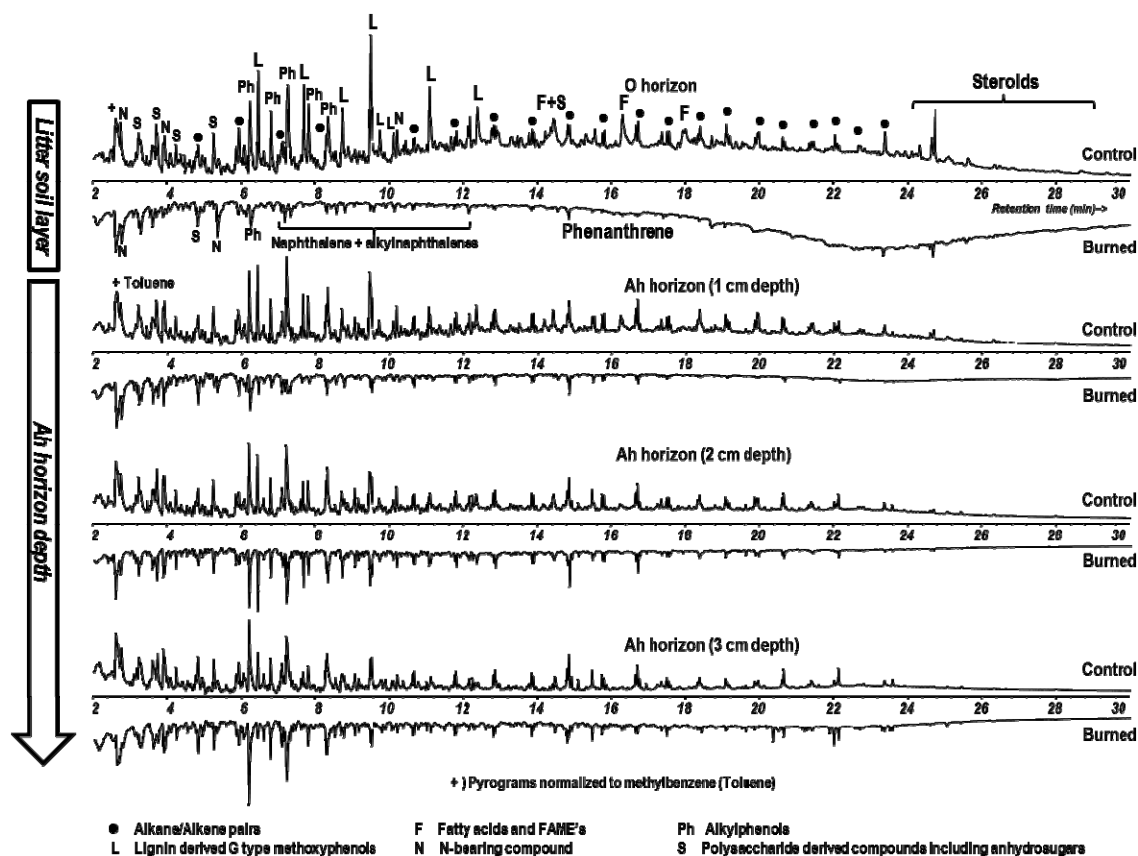
In this work the effect of fire to different soil properties and in particular to the quantitative and qualitative changes exerted to SOM are analysed in two different soil types; a gypseous soil (Hypergypsic Gypsisol) and a renzina (Rendzic Phaeozem). Undisturbed soil blocks sampled in the field were burned, under controlled conditions in the laboratory mimicking the conditions of a real wildfire.

With respect to C quantity, in general in the burned blocks a decrease in soil organic carbon (CO) was observed in the O horizon and down till the 1st cm in the mineral Ah horizon where a maximum temperature was 250 °C. No appreciable quantitative differences were observed in the inorganic C content (CI) at any depth.

With respect to C quality, soil organic matter alteration caused by fire was studied at a molecular level using direct analytical pyrolysis (Py-GC/MS). The technique was useful in assessing fire severity in terms of soil organic matter molecular structural shifts (Fig. 1). In the organic layer (O horizon) an almost complete disappearance of chromatographic peaks is apparent. In the mineral Ah horizon the effect of fire is still apparent (0-1 cm depth) affecting the chromatograms both qualitative and quantitative; a complete disappearance of some biogenic compounds, a reduction in the relative abundance of typical vegetation markers and a neat deviation of the natural distribution of the alkylic series i.e. shifts in carbon preference indexes (CPI) and increase in the relative abundance of low molecular weight homologues.

Among organic compounds, hydroaromatic structures (steroids) are found particularly resistant to heat, not only in the burned soils studied here, but also frequently observed by us to persists practically unaltered in other heavily charred matrices (biochars) obtained from a variety of substrates (LAR's, biomass, wood, etc.). The steroids are typical biomass markers with specific chemical structures informative

of origin i.e. vegetation, animals including humans, mosses or fungi. Several steroids and related compounds are well known physiologically active substances that play different roles in eukaryotic organisms. In the future it may be prudent to consider the potential effects of such substances when present in biochars, particularly when the intended use implies the release of large quantities into nature i.e. as amendments in



agriculture.

Figure 1. Total ion current chromatograms (TIC) of compounds released after pyrolysis (500 °C) of whole Hypergypsic Gypsisol (control vs. burned samples); axis x: retention time (min); axis y: relative abundance.

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TOTAL ORGANIC CARBON, TOTAL NITROGEN AND CHEMICAL CHARACTERISTICS OF AN HAPLIC CAMBISOL AFTER BIOCHAR INCORPORATION

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Biochar has been used as a soil conditioner to increase the soil organic carbon content and to improve the soil chemical characteristics. However, the effect of biochar on soil is still not clear and the soil type and biochar composition should also play an important role. In this context, the main objective of this work was to evaluate the effect of biochar application on the organic carbon (C) content and on chemical characteristics of subtropical Cambisol.

The field experiment was located at the State University of Centro-Oeste in Irati, Brazil, and the soil was classified as an Haplic Cambisol (Embrapa, 1999). The applied biochar was composed mainly by fine residues (70% < 2mm) of an eucalyptus biochar that was a waste of the local steel industry. In February 2010, four increasing doses of biochar were applied to the soil (T1 - 0 t ha⁻¹; T2 - 10 t ha⁻¹; T3 - 20 t ha⁻¹ and T4 - 40 t ha⁻¹) with four replicates. Soil samples were composed by three subsamples collected within each plot. Biochar was applied on the soil surface and thereafter it was incorporated into a 0 - 10 cm soil depth with an harrow. Soil samples were collected in September 2011 at four soil depths: 0 - 5; 5 - 10; 10 - 20 and 20 - 30 cm. The samples were air dried and passed through a 2 mm sieve. Soil C and nitrogen (N) contents were determined by dry combustion and the soil characteristics assessed were: pH in water, available P, exchangeable K, Ca, Mg and Al, potential acidity (H + Al), cation exchange capacity (CEC), effective cation exchange capacity (ECEC) and base saturation (V%) (Tedesco et al., 1995). The mean values were compared using SAS software (Tukey 10%).

The main alterations in soil characteristics were observed in the superficial depth (0 - 5 cm) (Table 1) probably due to the permanence of the biochar fine particles at the soil surface. In this layer, the application of 40 t ha⁻¹ of biochar (treatment T4) increased in 15.5 g kg⁻¹ the C content in comparison to treatment T1. The treatments T2 and T3 also increased the C content, but the differences were not significant. N content was not affected by biochar application. The highest dose of biochar (treatment T4) promoted an increase of the C/N ratio from 12 to 16 at the 0-5 cm depth. Treatment T4 also increased the soil pH value in comparison to treatment T1. In addition, the contents of available P, exchangeable K and Ca were higher under treatment T4 in comparison to treatment T1 (Table 1). In opposition, exchangeable Mg content, Al+H, V% and CEC were not altered by any treatment, but T4 increased the ECEC in 3.1 cmol_c dm⁻³ in comparison to T1. The results observed are probably due the high C and ash (26,5%) contents of biochar. A contribution of the functional groups on the surface of the biochar to the ECEC should not be excluded (Sparkes & Stoutjesdijk, 2011).

Our results indicate that after two years of biochar application an increase of soil organic carbon and a positive impact on the soil chemical characteristics at the soil surface were attained, but only with the highest tested dose (40 t ha⁻¹).

Table 1. Total organic carbon (TOC), total nitrogen (TN), C/N ratio, pH (H₂O), available P, exchangeable K, Ca, Mg and Al, potential acidity (H+Al), cation exchange capacity (CEC), effective cation exchange capacity (ECEC) and base saturation (V) of an Haplic Cambisol after incorporation of increasing doses of biochar.

Treatment	Depth	TOC	TN	C/N	pH(H ₂ O)	P	K	Ca	Mg	Al	H+Al	CEC	ECEC	V
	cm	g kg ⁻¹				mg dm ⁻³						cmol _c dm ⁻³		%
0 biochar	0 – 5	41.1 Ab	3.3 Aa	12.4	4.85 Ab	6.4 Ab	278.3 Ab	6.3 Ab	3.7 Aa	1.9 Da	20.0 Ba	30.6 Ba	12.5 Ab	37.3 Aa
	5 – 10	36.2 Ba	2.4 ABa	14.9	4.70 Ba	5.5 Ba	201.3 Ba	4.2 Ba	2.4 Ba	3.7 Ca	26.6 ABa	33.6 ABa	10.8 ABa	23.0 Ba
	10 – 20	29.3 Cb	2.1 Bab	13.7	4.50 Ca	4.3 Ca	149.5 BCa	2.7 Ca	1.3 Ca	5.3 Ba	35.2 Aa	39.6 Aa	9.7 Ba	11.8 BCa
	20 – 30	24.8 Da	1.9 Ba	12.8	4.43 Ca	3.0 Da	128.5 Ca	2.1 Ca	1.0 Ca	6.3 Aa	35.8 Aa	39.2 Aa	9.7 Ba	9.0 Ca
10 t ha ⁻¹	0 – 5	45.0 Ab	3.0 Aa	15.0	5.05 Aab	8.3 Ab	298.3 Ab	6.9 Aab	4.2 Aa	1.5 Cab	15.1 Ba	26.9 Ca	13.3 Aab	46.5 Aa
	5 – 10	36.9 ABa	2.5 Ba	15.1	4.80 Ba	5.5 Ba	206.0 Ba	4.5 Ba	2.8 Ba	2.7 Ca	21.3 Ba	29.1 BCa	10.5 Ba	28.3 ABa
	10 – 20	30.8 BCab	2.1 Bab	14.5	4.63 BCa	4.4 Ba	150.8 Ba	2.9 BCa	1.6 BCa	4.4 Ba	32.7 Aa	37.4 ABa	9.2 Ba	13.3 BCa
	20 – 30	28.3 Ca	2.0 Ba	14.9	4.55 Ca	3.9 Ba	136.3 Ba	1.8 Ca	1.1 Ca	6.1 Aa	35.8 Aa	39.1 Aa	9.4 Ba	8.3 Ca
20 t ha ⁻¹	0 – 5	46.0 Ab	3.1 Aa	14.8	5.05 Aab	7.3 Ab	338.0 Aab	7.2 Aab	4.4 Aa	1.1 Bab	14.0 Ba	26.5 Ba	13.5 Aab	48.3 Aa
	5 – 10	38.6 Ba	2.8 Aa	14.0	4.80 Ba	6.0 Ba	269.3 Ba	6.1 Aa	3.7 Ba	2.0 Ba	19.6 Ba	30.0 Ba	12.4 Aa	36.0 Ba
	10 – 20	31.4 Cab	2.1 Bb	15.3	4.63 Ca	5.2 Ca	177.5 Ca	3.6 Ba	2.1 Ca	4.0 Aa	33.0 Aa	39.1 Aa	10.2 Ba	17.0 Ca
	20 – 30	23.7 Da	1.8 Ba	13.3	4.53 Ca	3.5 Ca	134.8 Ca	2.4 Ca	1.4 Ca	5.6 Aa	36.2 Aa	40.3 Aa	9.7 Ba	11.0 Ca
40 t ha ⁻¹	0 – 5	56.6 Aa	3.5 Aa	16.2	5.20 Aa	11.8 Aa	391.3 Aa	9.1 Aa	4.9 Aa	0.7 Cb	12.1 Ca	27.1 Ca	15.6 Aa	56.3 Aa
	5 – 10	40.8 Ba	2.8 Ba	14.7	4.75 Ba	5.5 Ba	278.0 Ba	4.8 Ba	2.6 Ba	3.0 Ba	25.8 Ba	33.9 BCa	11.1 Ba	25.3 Ba
	10 – 20	36.0 Ba	2.4 BCa	15.3	4.60 BCa	4.5 Ba	174.0 Ca	3.2 Ca	1.6 Ca	5.0 Aa	35.2 Aa	40.4 ABa	10.2 Ba	14.0 Ca
	20 – 30	28.8 Ca	2.0 Ca	14.8	4.50 Ca	3.3 Ba	120.3 Ca	2.8 Ca	1.4 Ca	5.3 Aa	37.0 Aa	41.5 Aa	9.8 Ba	12.5 Ca

Means with the same capital letter do not differ within the same treatment and means with the same lowercase letter do not differ within depth (Tukey test, p < 0.10)

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THE EFFECTS OF BIOCHAR AMENDMENT ON SOIL EROSION AND INFILTRATION

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Through changing soil structure, biochar is expected to affect soil hydrology, both in terms of infiltration and run-off and erosion. Research up to date is scarce and has shown contradictory results (Buschner et al., 2010; Tryon, 1948; Verheijen et al., 2010). We will present the results of a pilot study that aims to identify if biochar mixed into soil affects the soil hydrology (infiltration and runoff), and if these effects correlate changes in soil structure. A 'perforated tray rotating disc type rainfall simulator' will allow for collecting both the run-off and the water percolated through the soil from a series of replicated rainfall simulation experiments (RSEs), under controlled conditions. Both types of water samples will be analysed for particle size (soil and biochar). The water samples will also be analysed for turbidity with a new plastic optical fibre-based sensor (Bilro et al. 2010), which has been developed at the University of Aveiro. The infiltration rate will be calculated from the measured percolated water.

The working hypotheses are: i) the contrasting soils have different relationships between biochar concentration and soil hydrology (infiltration/erosion); ii) water samples with suspended biochar will require modified calibration values for optical turbidity sensing.

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ASSESSMENT OF EFFECTS IN THE GERMINATION AND AGRONOMIC PRODUCTION OF FOUR CONTRASTING BIOCHARS. AN INCUBATION STUDY

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Considering the increasing amount of organic agricultural and urban wastes, there is a strong necessity for finding a sustainable strategy which allows managing and reducing these kinds of residues. In this sense, biochar has become more and more important and it has been proposed as a novel tool to achieve this goal. At the same time, this approach provides other benefits such as mitigate the climate change and enhance soil quality and plant growth. Different studies have reported the beneficial effects of using biochar as amendment in agricultural soils (Baronti et al., 2009). Biochar improves retention of nutrients and provides refugia for beneficial soil micro-organisms as well as increases pH, electrical conductivity and cation exchange capacity of soil. All of this makes biochar a suitable product to enhance agriculture productivity at the same time biochar contains large amounts of C. Thus, when applied to land, they have the potential to significantly, increase soil organic matter (SOM) contents, an aspect that is in critical decline in many regions of the world, particularly in Mediterranean ecosystems. However, great differences in biochar performance have been observed. Biochar properties depend on raw material and pyrolysis conditions, and not all biochars have demonstrated improved agricultural productivity in all cases (Gaskin et al., 2010; Van Zwieten et al., 2010), in addition negative effects at high application rates have been also observed (Baronti et al., 2009).

The aim of this study was to evaluate the effect of the application in a typical Mediterranean agricultural soil of four contrasting biochars produced from different feedstocks. The three biochars supplied by the European Biochar Research Network & COST Action TD1107 consisted of a) wood biochar, b) paper-sludge-bran biochar, c) sewage-sludge biochar. In addition "Bodegas Torres Company, Spain" provided the sample d) of grapevine wood biochar. This experiment was carried out in a greenhouse under similar conditions than those reported by De la Rosa et al 2013. Briefly they consisted of adjusting the soil humidity to 55% of the maximal water holding capacity, 25 °C for 79 days (14 h light day⁻¹) and water supply equivalent to 800 mm yr⁻¹ in quadruplicate. The bottom of the jars was perforated to allow leaching of surplus water. Finally, forty seeds of "*lolium perenne*" grass per pot were placed and amounts equivalent to 10, 20 and 40 T Ha⁻¹ were added. Control experiments (without biochar amendment) were also settled for comparison purposes. The germination toxicity, in terms of plant-survival (number of alive plants), and biomass production were measured after 6, 8, 10, 16, 23, 30, 37, 51, 65 and 78 days of incubation. Therefore, the shoots were accounted, cut, dried (48 h at 40 °C) and weighed at each of those intervals.

Results released from this experiment confirmed that beneficial effects of biochar in agriculture vary according to the kind of biochar used and its application rates.

Germination and plant-survival increased significantly in the cases of wood biochar and sewage-sludge biochars (samples a and c respectively). However, grapevine wood biochar resulted in similar germination rates than un-amended pots.

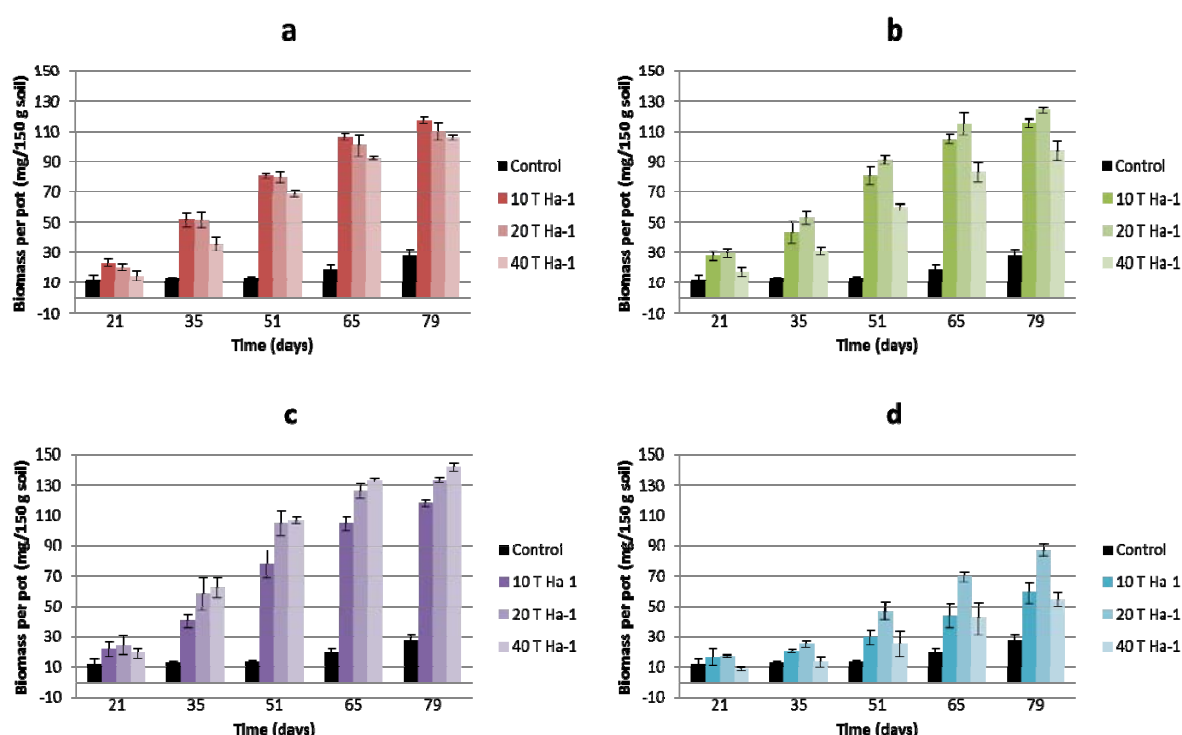


Figure 1. Cumulative agronomic productivity. (a) wood biochar, (b) paper-sludge-bran biochar, (c) sewage-sludge biochar, (d) grapevine wood biochar.

In addition, biomass production raised significantly in presence of all biochars (Fig. 1), being the response in presence of biochars a-c significantly higher than the response in presence of biochar d. Thus, according to this experiment biochar d can be considered to have no significant effect at short term compared to un-amended pots. However, the fate that production rates of this biochar by the end of the experiments are still raising could be indicative of potential beneficial effect at a longer term. Regarding the application rates, the biomass production was significantly increased for all doses when comparing to the control pots. Excepting biochar c, the application rates of 10 and 20 T Ha⁻¹ produced a major agronomic effect than 40 T ha⁻¹, which suggests a possibly harmfulness effect of biochar at high application doses.

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CHARCOAL INPUT INCREASES C SEQUESTRATION POTENTIAL OF SUBSOILS IN UMBRIC FERRALSOLS

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Climatic conditions of subtropical and tropical regions support fast carbon (C) mineralization, and thus an accelerated degradation of soil organic matter (SOM) if compared to temperate region. However, even in those regions, there are still soils that show notable C accumulation even in the deeper horizons. Examples for the latter are umbric horizons in typical tropical soils, such as Ferralsols. The occurrence of this soils with thick umbric epipedons (≥ 100 cm thickness) in areas of South Brazil still needs a better understanding, since the processes that are responsible for the thickness and darkness of the umbric horizons are of special interest with respect to the role of soils as carbon sink. Many of those soils are characterized by frequent fires caused by human activity during the last centuries and millennia. However, to which extend those fires and the subsequent input of charcoal affect the quality of the SOM or are responsible for the typical features of those soils is still not well understood.

In order to bring some light onto this issue, SOM from profiles of Umbric Ferralsols from Atibaia, Campinas (São Paulo State) and Chapecó (Santa Catarina State) developed under different environmental conditions were characterized by solid-state NMR spectroscopy. Their respective pyrogenic organic matter (PyOM) content was elucidated after their chemical oxidation with acid potassium dichromate and the quantification of chemical oxidation resistant aromatic carbon (COREC_{arom}). In order to reveal possible interaction with the mineral phase, iron and aluminium oxides were extracted with different extracting solutions (sodium pyrophosphate, ammonium oxalate and dithionite-citrate-bicarbonate solution) and related to SOM quality and quantity.

As it is typical for such soil, SOM concentrations in the A horizons of the studied soils are about times higher than those of other Ferralsols. Pyrogenic organic matter (PyOM) was identified down to the 2 meters depth. Interestingly, PyOM contributions were less in the top soils than in the deeper horizons, most tentatively because of efficient charcoal oxidation at the surface and the subsequent removal of the degradation products by further mineralization or by transport to deeper soil regions. According to solid-state NMR spectroscopy, the SOM of several deeper horizons was almost exclusively composed of PyOM. This observation demonstrates its preferential preservation in deep soils, possibly supported by its stabilization through the mineral phase. However, no correlation was revealed between clay content and aromatic C concentration. Only a weak relationship between aromaticity and content of Al and Fe-oxides was found indicating that

additionally to interaction between PyOM and mineral phase further mechanisms are involved in the preservation of PyOM in the deeper horizons.

A possible scenario which could explain the SOM distribution pattern in the examined soil may be that after initial oxidation of the charcoal in the topsoil, the residues were displaced either by leaching with the soil solution or by bioturbation along the profile. The low microbial activity and O₂ depletion in the deeper soil regions may have prevented or at least slowed down further O₂-requiring degradation of aromatic structures. Likely, this was contributing to the relatively high organic C concentrations in the subsoils of the studied umbric Ferralsols. Because the metabolization of carbohydrates, peptides and fatty acids is less effected by low oxygen availability, the PyOM was selectively preserved.

In summary our data clearly support that frequent charcoal addition can have a long-term impact on both the quality and quantity of organic matter in particular of deeper soil horizons. Here the oxidized PyOM is selectively preserved and seems to play a key role for increasing the amount of sequestered C in fire affected soils.

PRIMING EFFECT AFTER ADDITION OF PYROGENIC CARBON IN A SANDY SOIL MATRIX

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Pyrogenic carbon (C) is produced from different sources of biomass and by different pyrolysis processes. These two factors may not only affect the decomposition of pyrogenic C in soil but also the decomposition of the native soil organic matter (SOM). There are several studies on the decomposition rate of pyrogenic C and native SOM, and their interaction, however their results are conflicting. This study aimed to investigate the effect of biomass type on pyrogenic C and native SOM decomposition rate in a sandy soil.

Three feedstocks (*Glycine max* - i.e. Soybean; *Ricinus communis* - castor bean and; *Jatropha* sp) were pyrolysed by the low-temperature conversion (LTC) pyrolysis process and their pyrogenic C characterized for elemental (CHN) and structural (¹³C nuclear magnetic resonance (NMR) spectroscopy) composition. The decomposition rate was measured by CO₂ evolution and each source of CO₂ released was distinguished by the CO₂-¹³C signatures, because native SOM was dominated by the signature of C₄-plants.

The *Ricinus communis* seed and *Jatropha* cake had a higher C:N ratio than the soybean seed pyrogenic C. All pyrogenic C were rich in aromatic groups. Total amount of C relative in CO₂-C emitted ranged from 0.0263 g to 0.1112 g of CO₂-C for *Jatropha* cake and for *Ricinus communis* seed pyrogenic C, respectively. The final ¹³C signal (Table 1), was closer to that of pyrogenic C than to SOM and suggests preferential C degradation of the C₃ pyrogenic C against of SOM of the C₄ soil.

Table 1. The ¹³C signatures of sources and CO₂-C emitted, and the % C relative from each source in the CO₂-C emitted

Treatments	Sources	CO ₂ -C emitted	Pyrogenic C	Soil
	-----($\delta^{13}\text{C}$)-----		-----% C relative in CO ₂ -C emitted-----	
<i>Ricinus communis</i>	-26.60	-23.025	68.88-64.50	35.50-31.12
<i>Jatropha</i> sp.	-27.03	-22.268	60.05-54.69	45.31-39.95
<i>Glycine max</i>	-26.51	-22.373	63.71-58.58	41.42-36.29
Soil	-15.11	-16.520		100

Matching the CO₂-flux with the ¹³C signal indicated that the decomposition of pyrogenic C and of SOM was not simple additive processes (Figure 1), but that pyrogenic C reduced the decomposition of SOM (negative priming).

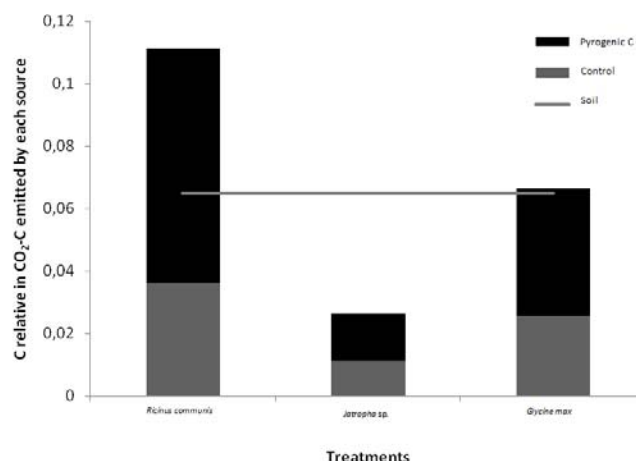


Figure 1. The negative priming effect of pyrogenic C application. Shown values are in accordance to the median values of the C relative in CO₂-C emitted by each source.

CONCLUSIONS

Our results showed (i) differences in the C:N ratio and chemical groups of the three pyrogenic C; (ii) differences in CO₂ evolution between treatments and control; (iii) preferential decomposition of compounds present in the pyrogenic C against the native SOM in soil and; (iv) samples richer in amorphous alkyl groups presented a higher decomposition rate of pyrogenic C than samples richer in aryl groups, indicating a preferential decomposition of these aliphatic compounds. As a main conclusion the application of pyrogenic C in this sandy soil resulted in an substantial early negative priming effect in the decomposition of native SOM.